

ANALYSIS OF SUB-MICRON MINERAL MATTER IN COAL VIA SCANNING TRANSMISSION ELECTRON MICROSCOPY*

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The mineral matter present in coal plays a deleterious role during the combustion of pulverized coal fuel in power generating boilers. Recent papers (1-3) on such problems as heat exchanger fouling and the emission of particulate pollutants from boilers have indicated that a fundamental understanding of these problems (and hence clues as to how they may be mitigated) may not depend solely on analyzing the fraction of mineral matter in the coal and its gross chemical composition. It may also prove necessary to obtain data on the actual size distribution of the original mineral particles and inclusions, and the distribution of these minerals among the particles of the pulverized fuel.

Such detailed information cannot be obtained by the traditional means of coal minerals analysis. However, recent advances in electron optical instrumentation and techniques, such as the use of a scanning transmission electron microscope (STEM) for high spatial resolution chemical microanalysis, show great promise for this type of characterization and have already been applied to coal research (4-7). The present work involves the use of a STEM both to obtain quantitative information about the ultra-fine (<100nm diameter) mineral inclusions present in several coals, and to examine the inorganic elements (hereafter referred to as inherent mineral matter) atomically bound into the organic matrices of these coals. It is anticipated that this type of information will be useful in modeling the combustion of pulverized fuel particles.

Sample Preparation

Samples of three different coals were examined in the present study: A lignite from the Hagel Seam in North Dakota, a semianthracite from the #2 Seam in Pennsylvania, and a sample of pulverized bituminous coal obtained courtesy of the Tennessee Valley Authority. The gross inorganic chemical analyses of the high temperature ash (HTA) of these three coals is shown in Table I.

Preparation of specimens for STEM examination was straightforward. Samples of each coal were ground to a fine powder using a mortar and pestle (except for the fuel coal which was already in pulverized form). A standard 3mm diameter 200 mesh copper transmission electron microscope grid coated with a thin carbon support film was then dipped into the powdered coal. Upon removal the grid was tapped several times to shake off excess and oversize particles. The final result was a sample consisting of a thin dispersion of fine coal particles clinging to the carbon support film.

Specimens prepared in this manner are well suited for STEM viewing and have several advantages compared to specimens thinned from the bulk by microtoming or ion milling. Their most notable advantage is of course the ease of preparation. Along with this, since nearly all the particles clinging to the grid have at least some area transparent to the electron beam, a much greater amount of thin area more randomly dispersed in origin from within the coal is potentially available for STEM examination than would be found in specimens thinned from bulk samples. Results obtained from powdered coal specimens should therefore be more representative of the overall mineral content of the initial coal sample.

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Table I: Compositions of High Temperature Ash (HTA)

Coal Name	Hagel Seam*	Cumberland Fuel**	Pennsylvania #2 Seam*
Coal Rank	Lignite	High Volatile	Semianthracite
%HTA	9.66	18.8	30.74
SiO ₂ (%)***	28.20	51.3	80.00
Al ₂ O ₃ (%)	9.35	19.8	12.10
TiO ₂ (%)	0.58	0.2	3.09
Fe ₂ O ₃ (%)	8.20	17.0	1.47
MgO(%)	5.91	1.2	0.05
CaO(%)	24.50	4.9	0.30
Na ₂ O(%)	2.81	0.9	0.05
K ₂ O(%)	0.33	2.8	0.35
P ₂ O ₅ (%)	0.10	0.2	0.05
SO ₃ (%)	17.40	1.6	0.30
Trace Elements	Ba-6700	Not	None
>1000ppm of HTA	Sr-3150	Available	Reported
(in ppm of HTA)			

*Information courtesy of the Penn State Coal Data Base

**Information taken from reference (8).

***%a - oxide % of HTA of dry coal

Experimental Procedure

The STEM used in the present study was a JOEL 200CX equipped with a Tracor-Northern TN2000 energy dispersive spectrometry (EDS) system for x-ray analysis. The features of STEM operation pertinent to this work are illustrated in Figure 1. The sample was illuminated by a narrow probe of 200kV electrons which was scanned across its surface. Transmitted electrons were used to form an image of the sample volume being scanned. The probe could also be stopped and fixed on some feature of interest in the sample, at which point the characteristic x-rays emitted by the atoms under the probe could be analyzed to obtain chemical information from a sample region with a diameter approaching that of the probe diameter. Chemical characterization could be accomplished in this manner for all elements with atomic number $Z \geq 11$.

For studies of mineral matter embedded in particles of powdered coal, advantage was taken of the difference in image contrast between the crystalline mineral particles and the surrounding amorphous organic matrix. The crystalline particles are capable of diffracting electrons, and so appeared in strong contrast when held at specific angles to the incident electron beam. The sample thus needed only to be tilted through some moderate range of angles (generally $\pm 45^\circ$ from the horizontal) to quickly establish the locations of the minerals within a given coal particle. During the tilting such particles abruptly "winked" in and out of strong diffraction contrast, while the amorphous matrix changed contrast only gradually as a function of the change in sample thickness intercepted by the electron beam. An example of an image of a mineral particle visible by strong diffraction contrast amidst an amorphous coal matrix is shown in Figure 2. It is estimated that the imaging procedure could detect mineral particles with diameters $> 2\text{nm}$. Particles smaller than this would most likely remain indistinguishable from the amorphous matrix.

With the location of an embedded mineral particle thus determined, the probe was fixed on the mineral and an x-ray spectrum was acquired. Except in the instance where the mineral extended through the full thickness of the coal particle intercepted by the probe, this spectrum consisted of a superposition of a particle spectrum and a matrix spectrum. To determine the signal associated with the inclusion, the probe was subsequently moved 1-2 particle diameters away to a region of the matrix known to be free of other minerals (within the resolution limitation

discussed in the preceeding paragraph), where a second spectrum was collected. Comparison of the two x-ray spectra generally quickly revealed the primary elemental constituents of the mineral (again, for elements of atomic number $Z \geq 11$). Two examples of this type of analysis are shown for a Ti-rich particle in the Cumberland fuel coal in Figure 3, and a particle rich in Ba and S in the Hage1 Seam coal in Figure 4.

Results and Discussion

The results of the STEM examination of the three coals are summarized in Table II. The first half of the table deals with the data obtained in a random sampling of mineral inclusions with mean diameters $<100\text{nm}$ which were found embedded in the coal particles. Quantitative results are presented for the two most frequently observed mineral types in this size range for each of the three starting coals.

The second half of the table describes the results of the matrix measurements which were undertaken concurrently with the particle analyses. Aside from being necessary to correctly identify the constituents associated with the discrete mineral particles, the matrix spectra themselves provided additional information on the inherent mineral elements atomically bound into the organic coal matrix, without the danger of confusion from elements in discrete mineral particles (at least for particles larger than $\sim 2\text{nm}$ in size). Recent work has suggested that such inherent mineral matter may comprise $>15\%$ of the total mineral matter in pulverized fuels (8).

Table II: Results of STEM Analysis

Coal Name	Hage1 Seam	Cumberland Fuel	Penn.#2 Seam
Total # of Particles Analyzed (dia. $<100\text{nm}$):	29	30	27
Predominant Particle Types*			
Major Elements	Fe	Ti	Ca
Number Observed	15	14	11
Average Diameter (nm)	43+17	45+22	45+27
Possible species**	-	TiO ₂ (Rutile)	CaCO ₃ (Calcite)
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Major Elements	Ba,S	Ca	Ti
Number Observed	7	5	10
Average Diameter(nm)	60+28	50+17	36+13
Possible species**	BaSO ₄ (Barite)	CaCO ₃ (Calcite)	TiO ₂ (Rutile)
# of Different Matrix Areas Analyzed:	25	21	24
Most Common Signal From Organic Matrix:	Ca	Si, Al	S
Frequency of Observation of Most Common Signal (% of Total # of Areas Analyzed):	96%	90%	42%
Frequency of Observation of S Signal from Matrix (% of Total # of Areas Analyzed):	28%	43%	42%

*The two most frequently observed particle types for particles with mean diameters $<100\text{nm}$. Categorization into types is based on major elements ($Z \geq 11$) observed in x-ray spectra attributable to particles.

**Tentative identification based on major elements ($Z \geq 11$) found in spectra. Species listed are the most common minerals found in coal which could produce the observed spectra. No clear choice exists for the Fe-rich particles in the lignite.

For all three coals, the predominant mineral species observed in the $<100\text{nm}$ size range would not be predicted from the results of the chemical analyses of the high temperature ash of the coals. None of the major elements ($Z>11$) observed (with the exception of sulfur in the Ba,S-rich particles) constitutes more than 10% of the HTA for the respective coals; indeed, Ba in the lignite, Ti in the bituminous coal, and Ca in the semianthracite all make up less than 1% of the respective ashes. Encountering these elements as the major constituents in the predominant mineral species observed in a random sampling of particles $<100\text{nm}$ in diameter indicates that the distribution of inorganic elements must not be uniform over all size ranges of mineral inclusions. In particular, for all three coals, the predominant mineral species observed in the $<100\text{nm}$ size range must therefore differ from those species predominating at larger size ranges.

In analyzing the background spectra obtained in this work, it was found that for two of the coals a particular element or combination of elements was observed in greater than 90% of all matrix measurements: Ca for the Hagel Seam lignite and a combination of Si and Al for the Cumberland bituminous. Examples of these two characteristic elemental signatures may be found in the two matrix spectra in Figures 3 and 4.

The semianthracite had no elements of $Z>11$ which were nearly as consistently observed in association with the matrix. In this coal, the most frequently observed matrix signal was from S, which only appeared in 42% of the observations. Indeed, in all three coals a S signal was detected in association with organic matrix, but only on an irregular basis (i.e., in less than 50% of the areas examined). Other elements, such as Fe, were also occasionally observed in the coal matrices. Such a point-to-point variation in inherent (atomically bound) mineral content may be expected to further complicate attempts to model the evolution of pulverized fuel particles into fly ash during combustion processes.

Conclusions

1. The STEM is an instrument well suited for the characterization of the sub-micron sized mineral matter in coal and can also be used to identify inorganic elements atomically bound in the organic coal matrix.
2. For the three coals studied, a random survey was taken of mineral inclusions $<100\text{nm}$ in mean diameter observed within coal particles in powdered coal samples. The results indicate that the predominant mineral species making up these inclusions differ from those species predominating in mineral particles at larger size ranges.
3. Two of the coals examined showed characteristic matrix "signatures" of inorganic elements which were observed in $>90\%$ of the matrix areas examined. The third coal did not. All three coals exhibited various elements with $Z>11$, most notably S, which were only irregularly associated with the matrix signal (i.e., found $<50\%$ of the time).

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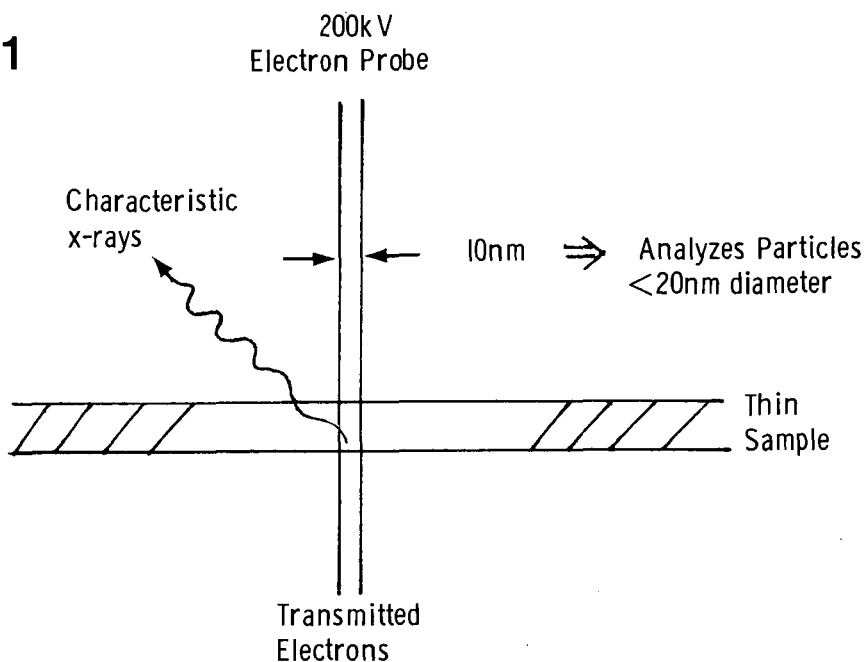


Figure 1: Schematic diagram of STEM operation during chemical microanalysis.



Figure 2: A transmitted electron image of a portion of a coal particle from the bituminous sample. A mineral inclusion is visible in strong diffraction contrast at A.

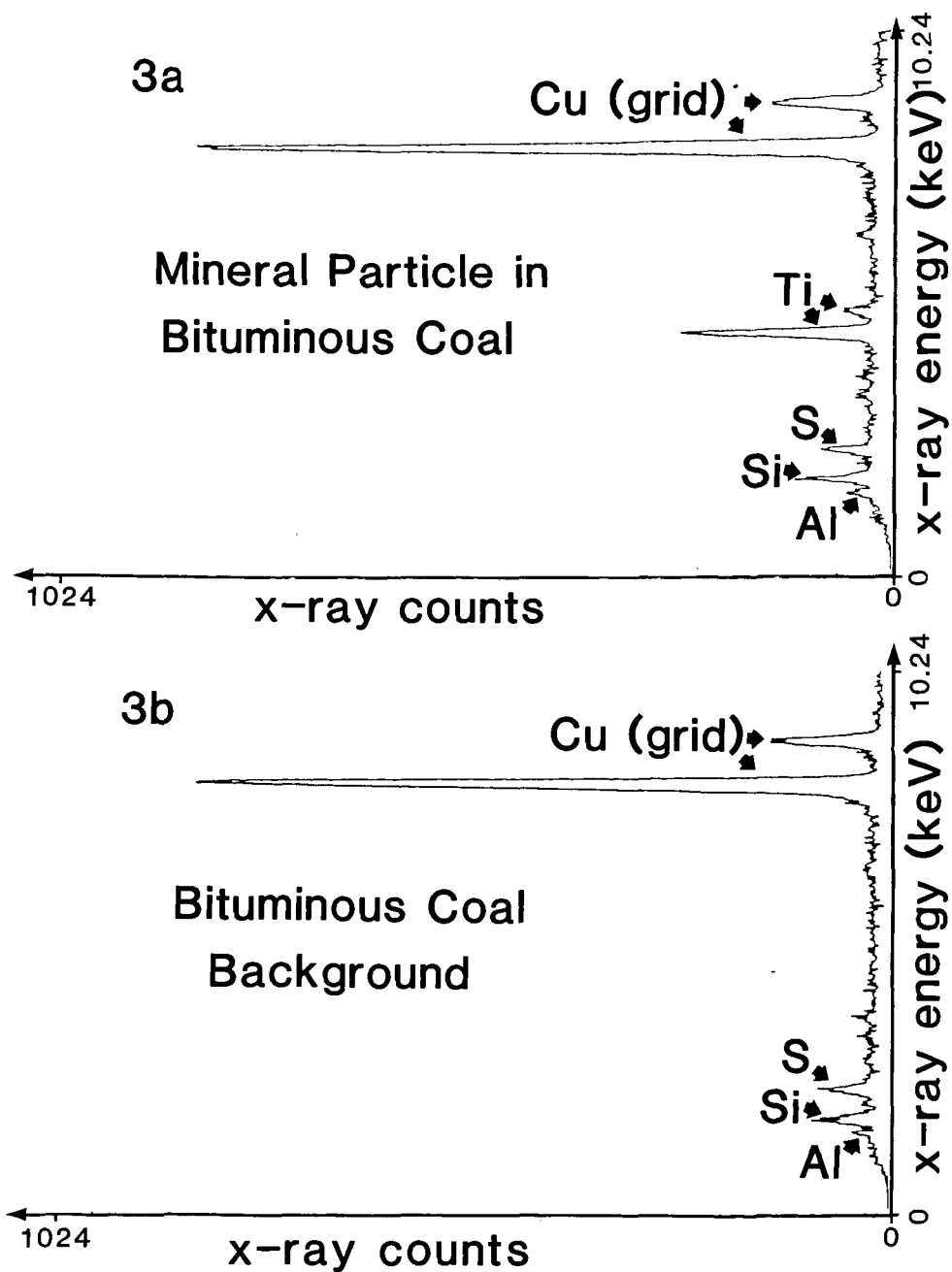


Figure 3: Examples of x-ray spectra from the bituminous sample.
a. Spectrum from particle shown in Figure 2.
b. Accompanying background spectrum.

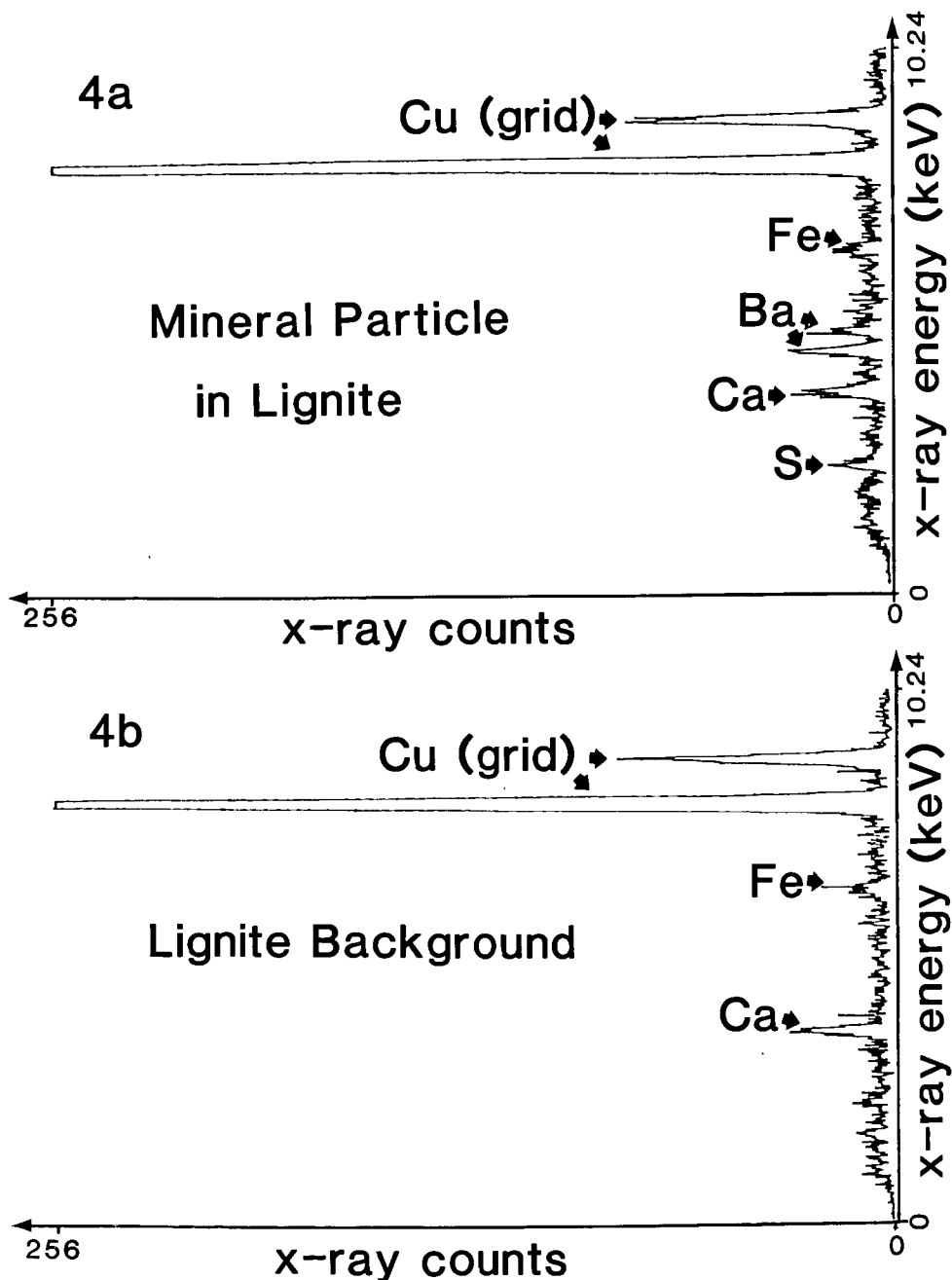


Figure 4: Examples of x-ray spectra from the lignite sample.
 a. Spectrum from 40nm diameter particle.
 b. Accompanying background spectrum.